

PCTWORLD INTELLECTUAL PROPERTY
International Bureau

WO 9608552A1

INTERNATIONAL APPLICATION PUBLISHED UNDER TI

(51) International Patent Classification ⁶ : C11D 3/08, 3/12		A1	(11) International Publication Number: WO 96/08552 (43) International Publication Date: 21 March 1996 (21.03.96)
(21) International Application Number: PCT/JP95/01750		(74) Agent: HOSODA, Yoshinori; Hosoda International Patent Office, Otemae M2 Building, 8-1, Tanimachi 2-chome, Chuo-ku, Osaka-shi, Osaka 540 (JP).	
(22) International Filing Date: 1 September 1995 (01.09.95)		(81) Designated States: CN, KR, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(30) Priority Data: 6/247279 13 September 1994 (13.09.94) JP		Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(71) Applicant (for all designated States except US): KAO CORPORATION [JP/JP]; 14-10, Nihonbashi Kayabacho 1-chome, Chuo-ku, Tokyo 103 (JP).			
(72) Inventors; and			
(75) Inventors/Applicants (for US only): YAMAGUCHI, Shu [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). USHIO, Nociaki [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). ISHIKURA, Akiko [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). KASAI, Katsuhiko [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). TSUMADORI, Masaki [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP). YAMASHITA, Hiroyuki [JP/JP]; Kao Corporation, Research Laboratories, 1334, Minato, Wakayama-shi, Wakayama 640 (JP).			

(54) Title: **WASHING METHOD AND CLOTHES DETERGENT COMPOSITION**

(57) Abstract

The clothes washing method using a phosphorus-free clothes detergent composition including a surfactant, an alkali metal silicate, and a metal ion capturing agent other than the alkali metal silicate, the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate being not more than 5/1, the method having the step of washing clothes in a washing liquid having the following washing conditions: (1) the washing liquid having a pH of not less than 10.60; (2) the washing liquid containing a material having an ion capturing capacity in an amount sufficient for theoretically changing a water hardness of water for washing to be not more than 0.5 °DH; and (3) the washing liquid having a surfactant concentration of from 0.07 to 0.17 g/L.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LJ	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

- 1 -

DESCRIPTION

WASHING METHOD AND CLOTHES DETERGENT COMPOSITION

TECHNICAL FIELD

5 The present invention relates to a washing method and a phosphorus-free clothes detergent composition. More specifically, the present invention relates to a washing method capable of having excellent washing power with a low surfactant concentration in the washing liquid and a 10 small amount of dosage, and a clothes detergent composition capable of achieving given washing conditions with a small amount of dosage thereof.

BACKGROUND ART

15 Various kinds of chelating agents, ion exchange materials, alkalizers, and dispersants have been known to be used for builders to be blended in detergents. Since the phosphate-based chelating agents having tripolyphosphates as a main component thereof have good 20 water solubility and washing power, they are used to be mainly employed.

25 In recent years, the use of tripolyphosphates has decreased, since they can cause eutrophication in closed freshwater areas such as lakes and marshes. Instead, crystalline aluminosilicates (zeolites), typically those

- 2 -

disclosed in Japanese Patent Laid-Open No. 50-12381, have been commonly used. In a detergent blend using the above zeolite, the standard amount of dosage for the detergent in Japan is generally about 40 g/30 L. Also, the powdery 5 detergents available at that time had low bulk density of from 0.20 to 0.45 g/ml from the viewpoint of solubility in cold water. As a result, the standard volumetric amount of dosage was about from 90 to 200 ml/30 L, which were extremely inconvenient for handling in distribution, at 10 stores and homes.

Therefore, an intense investigation has been made to produce compact detergents. For instance, Japanese Patent Laid-Open Nos. 62-167396, 62-167399, and 62-253699 disclose remarkable decrease in the amount of crystalline 15 inorganic salts such as sodium sulfate used as powdery aids conventionally contained in detergents. In addition, Japanese Patent Laid-Open Nos. 61-69897, 61-69899, 61-69900, and 5-209200 disclose that by increasing the bulk density of the detergents, to thereby have a bulk 20 density of from 0.60 to 1.00 g/ml, only a standard amount of dosage of 25 to 30 g/30 L is required, thereby making the detergents compact to have standard volumetric amount of dosage of from 25 to 50 ml/30 L.

25 However, in conventional detergents, a large amount

- 3 -

of surfactants had to be blended in the detergent compositions because mainstream of the technical idea was to make the oily components in dirt soluble by surfactants. Specifically, sebum dirt originated by human bodies which is the most typical dirt adhered to clothes, most likely to be observed on collars and sleeves, is taken as an example. The sebum dirt contains oily components, such as free fatty acids and glycerides, with a high content of not less than 70% (Ichiro KASHIWA et al., "Yukagaku," 19, 1095 (1969)). The oily components lock carbon and dirt in dust and peeled keratin, so that the resulting substance is observed as dirt. In order to wash off the sebum dirt, conventionally, detergents are designed based on a washing mechanism mainly by making these oily components soluble with micelle of surfactants, thereby detaching carbon, dirt, and keratin from clothes. This technical idea has been widely established among those of ordinary skill in the art, and even when the conventional detergents are shifted to compact detergents, substantially no changes took place in the surfactant concentration in the washing liquid. This fact is described in "Dictionary for Detergents and Washing," Haruhiko OKUYAMA et al., p. 428, 1990, First Edition, Asakura Publishing Company Limited, which shows that there are substantially no changes in concentrations in the

- 4 -

washing liquid for components other than sodium sulfate.

Based on these washing principles, the surfactant concentration in the washing liquid has to be made high in order to achieve high washing power, so that a large amount of surfactants has to be blended in the detergent composition. Therefore, a drastic reduction in the standard amount of dosage of the detergents was actually difficult. In addition, the presently known production method substantially enables to increase the bulk density to a level of about at most 1.00 g/ml. Therefore, a further reduction in the standard volumetric amount was deemed to be technically extremely difficult problem.

On the other hand, crystalline silicates having particular structure disclosed in Japanese Patent Laid-Open Nos. 5-184946 and 60-74595 shows not only good ion exchange capacity and actions of alkalizers (alkaline capacity). Therefore, possibility of more compact detergents has been investigated because both of the functions of two different components, including metal ion capturing agents, such as zeolites, and alkalizers, such as sodium carbonate, can be satisfied with the above crystalline silicates alone.

For instance, Japanese Patent Laid-Open No. 6-116588 is concerned with a detergent composition containing a crystalline silicate. In Examples of this publication

- 5 -

disclosing a more compact detergent, even in a case where the amount of the detergent composition at washing is reduced by 25%, the detergent composition has a washing power substantially the same as conventional detergent compositions. However, since the composition was formulated based on the conventional washing principle, the surfactant concentration was high, and the alkaline capacity and the ion exchange capacity were ascribed solely to the crystalline silicates contained therein. In this case, the functions of the crystalline silicates as alkalizers precede their functions as metal ion capturing agents, so that the washing power of the detergent composition was not always satisfactory. Therefore, if the amount of dosage of the detergent composition were reduced, a good washing power could not maintained.

A number of patent applications have been filed concerning the crystalline silicates disclosed in Japanese Patent Laid-Open NO. 60-74595. Japanese Patent Unexamined Publication No. 6-502199 discloses a detergent comprising a layered crystalline silicate, a zeolite, and a polycarboxylate in particular proportions, to thereby provide a detergent free from providing film layer formation on fibers and having excellent washing power and bleaching agent stability. However, under the blending conditions given in this publication, when the amount of

- 6 -

the detergents added was reduced at washing, the alkaline capacity is not sufficient because the amount of silicate in the builder composition is small, thereby making it impossible to maintain good washing power. Also, this 5 publication never teaches the technical idea that an excellent washing power is exhibited in a small amount of dosage of detergents.

The technical idea that an excellent washing power is exhibited in a small amount of dosage of detergents as in 10 the present invention cannot be found for detergents containing crystalline silicates disclosed in Japanese Patent Unexamined Publication 6-500141, Japanese Patent Laid-Open Nos 2-178398 and 2-178399. Rather, in the case where the amounts of the detergent compositions shown in 15 each of Examples are reduced, the washing power is lowered.

DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a 20 washing method with excellent washing power while having a low surfactant concentration by restudying a concept of the washing mentioned above.

Another object of the present invention is to provide a phosphorus-free clothes detergent composition suitably 25 giving characteristic washing conditions of the above

- 7 -

washing method, to thereby make it possible to wash clothes with the detergent composition with a considerably smaller standard amount of dosage than conventional compact laundry detergent products requiring about 25 to 5 30 g/ 30 liters.

In view of the above problems, the present inventors have studied the relationship between clothes washing conditions and washing power in an extremely simplified washing system. As a result, they have developed a novel 10 detergent composition which is sufficient for use in small amounts.

Specifically, after intensely studying the influence of the pH and the water hardness of the washing liquid to washing power, the present inventors have found the 15 following. The higher the pH is and the lower the water hardness is, the lower becomes the dependency of washing power on the concentration of the surfactant. In the case of high water hardness with high pH, the washing power drastically lowers in spite of high pH. Also, in the case 20 where a detergent containing a surfactant is used without adding an alkaliizer, the detergent has a low washing power at a low water hardness, but its washing power dependency on the water hardness becomes sufficiently lower than that of detergents containing alkaliizers. From the above 25 results, the present inventors have aimed at the

- 8 -

relationship between the washing liquid and dirt.

As explained in the prior art section, sebum stains, which are typical stains adhered to clothes, contain fatty acids and glycerides, the stains presumably being a mixture of these organic substances, carbon, and mud-dirt or keratin. When the washing liquid has a high pH, the content of the fatty acid increases due to a hydrolysis of glycerides, and the fatty acids proceed to form into salts with an alkali metal. Alkali metal salts of fatty acids are soaps by which suspension of dirt in the washing liquid is promoted. However, the reaction of the fatty acid forming a salt is a competitive reaction with calcium ions and magnesium ions in hard water. Since the alkali metal salts of fatty acids form scum with calcium ions and magnesium ions, in the case of high water hardness, the stains are solidified without being released from the interface with the cloth. From the above reasons, high pH and low water hardness of the washing liquid results in excellent washing power, and high water hardness of the washing liquid results in low washing power. In addition, in the case where an alkalizer is not included, since sebum stains are washed by the strength of the surfactant alone, dependency on the water hardness would be considerably smaller than those containing an alkalizer.

From the above phenomena, the present inventors have

- 9 -

found one of the reasons why the detergent composition is able to achieve substantially the same level or better washing power compared with conventional detergents while having a lower surfactant concentration than the 5 conventional ones. A soap obtained by saponifying the fatty acid in stains due to low water hardness and high pH acts to have excellent washing power, thereby making it possible to use a phosphorus-free clothes detergent composition with a smaller standard amount of dosage than 10 conventional detergents depending on surfactants. The present invention has been based upon these findings.

Accordingly, the gist of the present invention is as follows:

(1) A clothes washing method using a phosphorus-free 15 clothes detergent composition comprising a surfactant, an alkali metal silicate, and a metal ion capturing agent other than the alkali metal silicate, the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate being not more than 20 5/1, the method comprising the step of washing clothes in a washing liquid having the following washing conditions:

(1) The washing liquid having a pH of not less than 10.60;

(2) The washing liquid containing a material having 25 an ion capturing capacity in an amount sufficient for

- 10 -

theoretically changing a water hardness of water for washing to be not more than 0.5°DH; and

(3) The washing liquid having a surfactant concentration of from 0.07 to 0.17 g/L;

5 (2) The washing method described in (1) above, wherein the concentration of the detergent composition in the washing liquid is from 0.33 to 0.67 g/L for the water for washing with 2 to 6°DH;

10 (3) The washing method described in (1) above, wherein the concentration of the detergent composition in the washing liquid is from 0.50 to 1.20 g/L for the water for washing with 6 to 10°DH;

15 (4) The washing method described in (1) above, wherein the concentration of the detergent composition in the washing liquid is from 0.80 to 2.50 g/L for the water for washing with 10 to 20°DH;

(5) A phosphorus-free clothes detergent composition comprising components (a) to (c):

(a) a surfactant;

20 (b) an alkali metal silicate; and

(c) a metal ion capturing agent other than component (b),

wherein a total amount of (a), (b), and (c) components occupies 70 to 100% by weight of the entire composition,

25 and wherein the weight ratio of component (b) to component

- 11 -

- (a) is $b/a = 9/1$ to $1/2$, and the weight ratio of component (b) to component (c) is $b/c = 5/1$ to $1/15$;
- (6) The clothes detergent composition described in (5) above, wherein the weight ratio of component (b) to component (a) is $b/a = 9/1$ to $9/11$, and the weight ratio of component (b) to component (c) is $b/c = 4/1$ to $1/15$;
- (7) The clothes detergent composition described in (5) or (6) above, wherein the surfactant contains a nonionic surfactant in an amount of 50 to 100% by weight;
- (8) The clothes detergent composition described in (7), wherein the nonionic surfactant is a polyoxyethylene alkyl ether having an ethylene oxide moiety with an average molar number of from 5 to 15 and an alkyl moiety with average carbon atoms of from 10 to 18;
- (9) The clothes detergent composition described in any one of (5) to (8) above, wherein the alkali metal silicate is contained as an alkalizer in an amount of 50 to 100% by weight of the entire alkalizer;
- (10) The clothes detergent composition described in any one of (5) to (9) above, wherein the ratio of SiO_2/M_2O for the alkali metal silicate, M standing for an alkali metal, is from 0.5 to 2.6;
- (11) The clothes detergent composition described in any one of (5) to (10) above, wherein the alkali metal silicate is crystalline;

- 12 -

(12) The clothes detergent composition described in (11) above, wherein the crystalline alkali metal silicate is represented by the following formula (I):



5 wherein M stands for an element in Group Ia of the Periodic Table; Me stands for one or more elements selected from the group consisting of Group IIa, IIb, IIIa, IVa, and VIII; y/x is 0.5 to 2.6; z/x is 0.01 to 1.0; n/m is 0.5 to 2.0; and w is 0 to 20;

10 (13) The clothes detergent composition described in (11) above, wherein the crystalline alkali metal silicate is represented by the following formula (II):



15 wherein M stands for an alkali metal; x' is 1.5 to 2.6; and y' is 0 to 20;

16 (14) The clothes detergent composition described in any one of (5) to (13) above, wherein the (c) metal ion capturing agent contains a carboxylate polymer having a Ca ion capturing capacity of not less than 200 CaCO₃ mg/g in an amount of not less than 10% by weight;

17 (15) The clothes detergent composition described in any one of (5) to (14) above, wherein the (c) metal ion capturing agent comprises:

18 (c-i) a carboxylate polymer having a Ca ion capturing capacity of not less than 200 CaCO₃ mg/g; and

- 13 -

(c-ii) an aluminosilicate having an ion exchange capacity of not less than 200 CaCO₃ mg/g and having the following formula (III):



5 wherein M stands for an alkali metal; x'', y'', and w'' each stands for a molar number of each component; x'' is from 0.7 to 1.5; y'' is from 0.8 to 6.0; and w'' is from 0 to 20, and wherein the weight ratio of (c-i) component to (c-ii) component is (c-i)/(c-ii) = 1/20 to 4/1, and the total 10 amount of (c-i) and (c-ii) components occupies 70 to 100% by weight based on the (c) metal ion capturing agent; and (16) The washing method described in (1) above, wherein the clothes detergent composition described in any one of (5) to (15) above is used.

15

BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will become more fully understood from the detailed description given hereinbelow and the accompanying drawings which are given by way of 20 illustration only, and thus, are not limitative of the present invention, and wherein:

Figure 1 is a graph showing a calibration curve of the relationship between the logarithm of the calcium ion concentration and the voltage; and

25 Figure 2 is a graph showing the relationships between

- 14 -

the amount of samples added dropwise and the calcium ion concentration.

BEST MODE FOR CARRYING OUT THE INVENTION

5 The washing method of the present invention, using a phosphorus-free clothes detergent composition comprising a surfactant, an alkali metal silicate, and a metal ion capturing agent other than the alkali metal silicate, the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate being 10 not more than 5/1, is characterized by using a washing liquid having the following washing conditions:

 (1) The washing liquid having a pH of not less than 10.60;

15 (2) The washing liquid containing a material having an ion capturing capacity in an amount sufficient for theoretically changing a water hardness of water for washing to be not more than 0.5°DH; and

20 (3) The washing liquid having a surfactant concentration of from 0.07 to 0.17 g/L.

 Here, the washing conditions are given for washing liquids including no clothes to be washed.

 By setting the washing conditions as given above, the resulting washing power is excellent while having a low 25 surfactant concentration, thereby making the standard

- 15 -

amount of dosage of the detergents smaller than the conventional ones. When the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate exceeds 5/1, sufficient washing 5 power cannot be obtained even if the above conditions are satisfied.

In the washing method of the present invention, the preferred washing conditions for each of the washing conditions (1) to (3), are as follows.

10 (1') The washing liquid having a pH of from 10.85 to 11.00, more preferably from 10.90 to 11.00;

15 (2') The washing liquid containing a material having an ion capturing capacity in an amount sufficient for theoretically changing a water hardness of water for washing to be 0°DH, more preferably in an amount sufficient for theoretically giving so low a water hardness as -1°DH; and

20 (3') The washing liquid having a surfactant concentration of from 0.08 to 0.14 g/L, more preferably from 0.08 to 0.11 g/L.

In addition, the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate is preferably 4/1 to 1/15, more preferably 3/1 to 1/15.

25 Incidentally, a preference is given to those

- 16 -

satisfying all of the preferred washing conditions, but by satisfying one or more of the above preferred washing conditions, the effects of the present invention are markedly exhibited.

5 In addition, although a concrete specific amount of dosage, i.e. the detergent concentration in the washing liquid, depends upon the water hardness of the water for washing used, the additional or reduced amount thereof varies depending upon the amount of the metal ion capturing agent added. Therefore, the surfactant concentration in the washing liquid does not basically change thereby for the reasons set forth below.

10

15 The standard amount of dosage of the detergents greatly differs throughout the world. This is due to the differences in the water hardness of tap water in each of the countries. For instance, while the tap water has a water hardness of usually around 4°DH in Japan, the tap water having a water hardness of not less than 6°DH in the U.S., and that exceeding 10°DH in European countries is used for the water for washing. Therefore, since the required absolute amount of the metal ion capturing agent varies, the standard amount of dosage would be adjusted accordingly. In the present invention, although the amount of the metal ion capturing agent varies depending upon the water hardness, the surfactant concentration in

20

25

- 17 -

the washing liquid remains substantially the same, and the standard amount of dosage becomes smaller than the conventional ones.

Specifically, in cases where the initial water
5 hardness differs in each of the washing liquids, the detergent concentrations are as follows:

1) As for the water for washing having a water hardness of 2 to 6°DH, the detergent composition has a concentration in the washing liquid of from 0.33 to
10 0.67 g/L, preferably from 0.33 to 0.50 g/L.

2) As for the water for washing having a water hardness of 6 to 10°DH, the detergent composition has a concentration in the washing liquid of from 0.50 to 1.20 g/L, preferably from 0.50 to 1.00 g/L.

15 3) As for the water for washing having a water hardness of 10 to 20°DH, the detergent composition has a concentration in the washing liquid of from 0.80 to 2.50 g/L, preferably from 1.00 to 2.00 g/L.

Here, each of the above washing conditions are
20 measured by the following methods.

(1) The pH of the washing liquid is measured at 25°C by such devices as a conventional glass electrode pH meter.

(2) The amount of the materials having ion capturing capacity to be present in the washing liquid, i.e.,
25 amounts of the alkali metal silicates and the metal ion

- 18 -

capturing agents other than alkali metal silicates, is calculated as follows.

For instance, the amount corresponding to an ion capturing capacity required to theoretically change the 5 water hardness of the water for washing to 0.5°DH is calculated by calculating a concentration of Ca and Mg ions corresponding to the hardness difference from the water hardness of the water for washing used (for instance, in Japan the water hardness is about 4°DH), and 10 then obtaining a total calcium ion capturing capacity corresponding to the calculated ion concentration in terms of concentration units. In this case, the amount of the water for washing and the amount of the detergent composition added are so selected to satisfy the washing 15 condition (3) above where the surfactant concentration is from 0.07 to 0.17 g/L.

Here, the methods for measuring the ion capturing capability of the metal ion capturing materials depend upon whether the ion exchange materials or the chelating 20 agents are used for the metal ion capturing materials. The measurement methods for each of the materials are given below.

Ion Exchange Materials

A 0.1 g sample is accurately weighed and added to 25 100 ml of a calcium chloride aqueous solution (500 ppm

- 19 -

concentration, when calculated as CaCO_3), followed by stirring at 25°C for 60 minutes, after which the mixture is filtered using Membrane Filter (made of nitrocellulose; manufactured by Advantech) with 0.2 μm pore size. 10 ml 5 of the filtrate is assayed for Ca content by an EDTA titration, and the calcium ion exchange capacity (cationic exchange capacity) of the sample is calculated from the titer.

Examples of the ion exchange materials used for 10 measurement in the present invention include inorganic substances, such as crystalline alkali metal silicates and aluminosilicates (zeolites, etc.).

Chelating Agents

The calcium ion capturing capacity was measured by 15 the following method using a calcium ion electrode. Incidentally, the solution used herein was prepared with the following buffer solution:

Buffer: 0.1 M- NH_4Cl - NH_4OH solution (pH 10.0)

20 (i) Preparation of Calibration Curve

A standard calcium ion solution was prepared and used for obtaining a calibration curve showing the relationships between the logarithm of the calcium ion concentration and the voltage, as shown in Figure 1.

25 (ii) Measurement of Calcium Ion Capturing Capacity

- 20 -

About a 0.1 g sample was weighed into a 100 ml volumetric flask, and the volumetric flask was filled up to a volume of 100 ml with the above buffer solution. A CaCl₂ aqueous solution (pH 10.0) having a concentration of 5 20,000 ppm calculated as CaCO₃, was added dropwise from a burette in an amount of 0.1 to 0.2 ml for reading each sample voltage. A blank sample was also measured. Thus, a calcium ion concentration was calculated from the calibration curve given in Figure 1 by applying a sample 10 voltage. The calcium ion concentration of the upper line corresponding to the amount A of samples added dropwise shown in Figure 2 was referred to as calcium ion capturing capacity. Examples of the chelating agents used for measurement in the present invention include 15 polycarboxylates, such as citrates, and carboxylate polymers, such as acrylic acid-maleic acid copolymers.

The washing methods of the present invention are applicable to any one of the following cases.

- 1) The case where the water for washing has a water 20 hardness of from 2 to 6°DH;
- 2) The case where the water for washing has a water hardness of from 6 to 10°DH; and
- 3) The case where the water for washing has a water hardness of from 10 to 20°DH.

25 For all of these cases, the washing conditions (1) to

- 21 -

(3) above are similarly applicable, where only the detergent concentration is so selected for each water hardness 1) to 3) to satisfy the washing conditions (1) to (3).

5 As explained in the above washing method of the present invention, in order to produce a washing liquid having a high pH and a low water hardness, thereby exhibiting an excellent washing power, the washing liquid has to satisfy the following conditions.

10 (i) Containing excess metal ion capturing agents.
 (ii) Containing an alkaliizer capable of buffering at high pH.

Although crystalline silicates satisfying both (i) and (ii) above are known, much care is needed for the use 15 of the crystalline silicate for the following reasons. The increase in the amount of the crystalline silicates for lowering water hardness results in the increase the alkaline capacity. This in turn inevitably results in an undesirable increase in the exchanging speeds of the fatty acids for Ca and Mg. Therefore, in order to satisfy more preferred conditions, the metal ion capturing agents other than the alkali metal silicates are required to be added 20 in a given ratio. When the amount of these metal ion capturing agents other than the alkali metal silicates is 25 outside a given range, it would be difficult to reduce the

- 22 -

amount of the detergent used.

Accordingly, the phosphorus-free detergent composition of the present invention comprises components (a) to (c):

5 (a) a surfactant;
(b) an alkali metal silicate; and
(c) a metal ion capturing agent other than component
(b),

wherein a total amount of (a), (b), and (c) components
10 occupies 70 to 100% by weight of the entire composition,
and wherein the weight ratio of component (b) to component
(a) is $b/a = 9/1$ to $1/2$, preferably $9/1$ to $9/11$, and the
weight ratio of component (b) to component (c) is $b/c =$
5/1 to 1/15, preferably 4/1 to 1/15.

15 A greater preference is given to a detergent
composition containing the components (a) to (c) above,
wherein a total amount of (a), (b), and (c) components
occupies 80 to 100% by weight of the entire composition,
and wherein the weight ratio of component (b) to component
20 (a) is $b/a = 9/1$ to $1/1$, and the weight ratio of component
(b) to component (c) is $b/c = 3/1$ to $1/15$. Most
preferably, the weight ratio of component (b) to component
(c) is $b/c = 3/1$ to $3/7$, in the case where the water for
washing has a water hardness of from 2 to 6°DH ; or $b/c =$
25 $4/3$ to $1/6$, in the case where the water for washing has a

- 23 -

water hardness of from 6 to 10°DH; or b/c = 1/1 to 1/15, in the case where the water for washing has a water hardness of from 10 to 20°DH. In the present invention, by having the above composition, a detergent composition 5 having a remarkably smaller standard amount of dosage for each of the water for washing having different water hardness can be obtained.

Each of the components will be explained in detail below.

10

(a) Surfactant

The surfactants usable in the present invention are not particularly limited, and any ones generally used for detergents are used, in which a nonionic surfactant is 15 preferably contained in an amount of from 50 to 100% by weight, more preferably from 65 to 100% by weight, of the entire surfactant. Specifically, they may be one or more surfactants selected from the group consisting of nonionic surfactants, anionic surfactants, cationic surfactants, 20 and ampholytic surfactants, each being exemplified below. For instance, the surfactants can be chosen such that the surfactants of the same kind are chosen, as in the case where a plurality of the nonionic surfactants are chosen. Alternatively, the surfactants of the different kinds are 25 chosen, as in the case where the anionic surfactant and

- 24 -

the nonionic surfactant are respectively chosen.

Examples of the nonionic surfactants are as follows:

Polyoxyethylene alkyl ethers, polyoxyethylene
alkylphenyl ethers, polyoxyethylene sorbitan fatty acid
5 esters, polyoxyethylene sorbitol fatty acid esters,
polyethylene glycol fatty acid esters, alkyl polyethylene
glycol fatty acid esters, polyoxyethylene polyoxypropylene
alkyl ethers, polyoxyethylene castor oils, polyoxyethylene
alkylamines, glycerol fatty acid esters, higher fatty acid
10 alkanolamides, alkylglucosamides, alkylglucosides, and
alkylamine oxides.

Among the nonionic surfactants, a preference is given
to polyoxyethylene alkyl ethers which are ethylene oxide
adducts whose alkyl moieties are ascribed to linear or
15 branched, primary or secondary alcohols, each having 10 to
18 carbon atoms, and whose ethylene oxide moieties have an
average molar number of 5 to 15, and more preferably
polyoxyethylene alkyl ethers which are ethylene oxide
adducts whose alkyl moieties are linear or branched,
20 primary or secondary alcohols, each having 12 to 14 carbon
atoms, and whose ethylene oxide moieties have an average
molar number of 6 to 10.

Examples of the anionic surfactants include
alkylbenzenesulfonates, alkyl or alkenyl ether sulfates,
25 alkyl or alkenyl sulfates, α -olefinsulfonates,

- 25 -

α -sulfofatty acid salts, α -sulfofatty acid ester salts, alkyl or alkenyl ether carboxylates, amino acid-type surfactants, and N-acyl amino acid-type surfactants, with a preference given to alkylbenzenesulfonates, alkyl or 5 alkenyl ether sulfates, and alkyl or alkenyl sulfates.

Examples of the cationic surfactants include quaternary ammonium salts, such as alkyl trimethylamine salts. Examples of the amphotolytic surfactants include carboxy-type and sulfobetaine-type amphotolytic surfactants.

10 The surfactant content is preferably from 1 to 45% by weight, and the surfactant content is particularly in the following ranges, depending on the types of water for washing used.

- 15 1) In the case where the water for washing having a water hardness of 2 to 6°DH, the surfactant content is particularly preferably from 15 to 30% by weight;
- 2) In the case where the water for washing having a water hardness of 6 to 10°DH, the surfactant content is particularly preferably from 8 to 25% by weight; and
- 20 3) In the case where the water for washing having a water hardness of 10 to 20°DH, the surfactant content is particularly preferably from 5 to 20% by weight.

When the surfactant content is lower than the lower limit in each of the above given ranges, a sufficient 25 washing power of the detergent cannot be obtained, and

- 26 -

when the surfactant content exceeds the upper limit in each of the above given ranges, the amounts of the alkalinizers and the metal ion capturing agent are relatively lowered, making it less likely to obtain 5 sufficient washing power.

By having the above compositions for the clothes detergent composition of the present invention, when the detergent composition is so added to each of the water for washing to provide a surfactant concentration in the 10 washing liquid of from 0.07 to 0.17 g/L, the concentrations of the detergent composition in each of the washing liquid are as follows depending upon the types of the water for washing used.

- 1) In the case where the water for washing having a 15 water hardness of 2 to 6°DH, the concentration of the detergent composition in the washing liquid is from 0.33 to 0.67 g/L, preferably from 0.33 to 0.50 g/L;
- 2) In the case where the water for washing having a water hardness of 6 to 10°DH, the concentration of the 20 detergent composition in the washing liquid is from 0.50 to 1.20 g/L, preferably from 0.50 to 1.00 g/L; and
- 3) In the case where the water for washing having a water hardness of 10 to 20°DH, the concentration of the detergent composition in the washing liquid is from 0.80 25 to 2.50 g/L, preferably from 1.00 to 2.00 g/L.

- 27 -

Therefore, the standard amounts of dosage of the detergent composition of the present invention for obtaining a sufficient washing power are considerably smaller than the conventional compact detergent compositions.

5

(b) Alkali Metal Silicates

The alkali metal silicates usable in the present invention may be either crystalline or amorphous alkali metal silicates. A preference is given to crystalline alkali metal silicates for the following reasons. By forming crystalline alkali metal silicates, the silicates are provided with not only good alkaline capacity but also good ion exchange capacity, thereby making it possible to further reduce the standard amount of dosage of the detergent compositions.

10 Examples of the crystalline alkali metal silicates usable in the present invention include alkali metal silicates having an $\text{SiO}_2/\text{M}_2\text{O}$ ratio (wherein M stands for an alkali metal) of from 0.5 to 2.6. On the other hand, the crystalline silicates used in the reference explained in the prior art section have $\text{SiO}_2/\text{Na}_2\text{O}$ ratios of from 1.9 to 4.0. However, in the present invention, the silicates having $\text{SiO}_2/\text{Na}_2\text{O}$ ratios exceeding 2.6 would not give the 15 effects obtained in the present invention, making it

20

25

- 28 -

impossible to produce detergents capable of having an excellent washing power with only small standard amounts of dosage.

5 Among the crystalline alkali metal silicates usable in the present invention, a preference is given to those exemplified by having the following compositions (I) and (II) given below.

i) $xM_2O \cdot ySiO_2 \cdot zMe_nO_n \cdot wH_2O$, (I)

10 wherein M stands for an element in Group Ia of the Periodic Table; Me stands for one or more elements selected from the group consisting of Group IIa, IIb, IIIa, IVa, and VIII; y/x is from 0.5 to 2.6; z/x is from 0.01 to 1.0; n/m is from 0.5 to 2.0; and w is from 0 to 20.

15 ii) $M_2O \cdot x'SiO_2 \cdot y'H_2O$, (II)

wherein M stands for an alkali metal; x' is from 1.5 to 2.6; and y' is from 0 to 20.

First, the crystalline alkali metal silicates having the composition i) above will be detailed below.

20 In the general formula (I), M stands for an element selected from Group Ia of the Periodic Table, the Group Ia elements exemplified by Na, K, etc. The Group Ia elements may be used alone, or may constitute an M_2O component by blending such compounds as Na_2O and K_2O .

25 Me stands for one or more elements selected from the

- 29 -

group consisting of Group IIa, IIb, IIIa, IVa, and VIII of the Periodic Table, and examples thereof include Mg, Ca, Zn, Y, Ti, Zr, and Fe. Although not being particularly limited to the above examples, a preference is given to Mg 5 and Ca from the viewpoint of resource stock and safety. In addition, these elements may be used alone or may constitute an Me_nO_n component by blending such compounds as MgO and CaO.

In addition, the crystalline alkali metal silicates 10 usable in the present invention may be in the form of hydrates, wherein the amount of hydration (w) is normally in the range of from 0 to 20 moles of H_2O .

With respect to the general formula (I), y/x is from 0.5 to 2.6, preferably from 1.5 to 2.2. When y/x is less 15 than 0.5, the obtained composition has insufficient anti-solubility in water, thereby providing drastically poor caking ability, solubility, and other powder properties of the detergent composition. When y/x exceeds 2.6, the obtained composition has a low alkaline capacity, 20 thereby making it insufficient to be used as an alkaliizer, and it also has a low ion exchange capacity, thereby making it insufficient to be used as an ion exchange material. With respect to z/x , it is from 0.01 to 1.0, preferably from 0.02 to 0.9. When z/x is less than 0.01, 25 the obtained composition has insufficient anti-solubility

- 30 -

in water, and when z/x exceeds 1.0, the obtained composition has a low ion exchange capacity, making it insufficient to be used as an inorganic ion exchange material. With respect to x , y and z , there are no 5 limitations, as long as y/x and z/x have the above relationships. When xM_2O , for example, is $x'Na_2O \cdot x''K_2O$ as described above, x equals to $x' + x''$. The same can be said for z when $zMe_{n_0}O_n$ comprises two or more components. Further, "n/m is from 0.5 to 2.0" indicates the number of 10 oxygen ions coordinated to the above elements, which actually takes values selected from 0.5, 1.0, 1.5, and 2.0.

The crystalline alkali metal silicate in the present invention comprises three components, M_2O , SiO_2 , and $Me_{n_0}O_n$, 15 as indicated by the general formula (I) above. Materials which can be converted to each of these components, therefore, is indispensable for starting materials for producing the crystalline alkali metal silicate in the present invention. In the present invention, known 20 compounds can be suitably used for starting materials without limitations. Examples of the M_2O component and the $Me_{n_0}O_n$ component include simple or complex oxides, hydroxides and salts of respective elements; and minerals containing respective elements. Specifically, examples of 25 the starting materials for the M_2O component include NaOH,

KOH, Na₂CO₃, K₂CO₃, and Na₂SO₄. Examples of the starting materials for the Me_nO_n component include CaCO₃, MgCO₃, Ca(OH)₂, Mg(OH)₂, MgO, ZrO₂, and dolomite. Examples of the starting materials for the SiO₂ component include silica sand, kaolin, talc, fused silica, and sodium silicate.

In the present invention, a method of producing the crystalline alkali metal silicate may be exemplified by blending these starting material components to provide the desired compositions in x, y, and z for the crystalline alkali metal silicate, and baking the resulting mixture at a temperature in the range of normally from 300 to 1500°C, preferably from 500 to 1000°C, more preferably from 600 to 900°C, to form crystals. In this case, when the heating temperature is less than 300°C, the crystallization is insufficient, thereby making the anti-solubility in water of the resulting crystalline alkali metal silicate poor, and when it exceeds 1500°C, coarse grains are likely to be formed, thereby decreasing the ion exchange capacity of the resulting crystalline alkali metal silicate. The heating time is normally 0.1 to 24 hours. Such baking can normally be carried out in a heating furnace such as an electric furnace or a gas furnace.

The crystalline alkali metal silicate in the present invention thus obtained has a pH of not less than 11 in a 0.1% by weight dispersion solution, showing an excellent

- 32 -

alkaline capacity. Also, the crystalline alkali metal silicates particularly excels in their alkaline buffering effects, having excellent alkaline buffering effects when compared with those of sodium carbonate and potassium

5 carbonate.

The crystalline alkali metal silicate in the present invention thus obtained has an ion exchange capacity of not less than 100 mg CaCO₃/g, preferably 200 to 600 mg CaCO₃/g, which is one of the material having an ion

10 capturing ability in the present invention.

In the crystalline alkali metal silicate usable in the present invention, the amount of Si dissolved in water is normally not more than 110 mg/g, when calculated as SiO₂, which can be said to be substantially insoluble in

15 water. Here, the term "substantially insoluble in water" means stability in water of the chemical structure concerned with the cationic exchange capacity, so that the amount of Si dissolved, when calculated as SiO₂, is normally not more than 110 mg/g when a 2 g sample is added

20 to 100 g of ion exchanged water and the mixture is stirred at 25°C for 30 minutes. In the present invention, a preference is given to a case where the amount of Si dissolved is not more than 100 mg/g for the purpose of obtaining further excellent effects of the present

25 invention.

- 33 -

Since the crystalline alkali metal silicate usable in the present invention has not only good alkaline capacity and alkali buffering effects but also good ion exchange capacity, the above-mentioned washing conditions are 5 suitably adjusted by adding suitable amounts of the crystalline alkali metal silicate.

In the present invention, the crystalline alkali metal silicate usable in the present invention has an average particle size preferably of from 0.1 to 50 μm , 10 more preferably from 1 to 30 μm , still more preferably from 1 to 10 μm . When the average particle size of the crystalline alkali metal silicate exceeds 50 μm , the ion exchange speed thereof is likely to be slowed down, thereby resulting in the lowering of the detergency. In 15 addition, when the average particle is less than 0.1 μm , the specific surface area increases, thereby increasing the hygroscopic property and the CO_2 absorption property, which in turn makes it likely to cause drastic quality deterioration. Incidentally, the average particle size 20 referred herein is a median diameter obtained from a particle size distribution.

The crystalline alkali metal silicate having the average particle size and the particle size distribution mentioned above can be prepared by pulverizing the 25 material using such pulverizing devices as a vibrating

- 34 -

mill, a hammer mill, a ball-mill, and a roller mill. For instance, the crystalline alkali metal silicate can be easily obtained by pulverizing the material with a vibrating mill "HB-O" (manufactured by Chuo Kakohki Co., 5 Ltd.).

The content of the crystalline alkali metal silicate is preferably 4 to 75% by weight in the entire composition, with a particular preference given to the following compositions depending upon the water hardness 10 of the water for washing used.

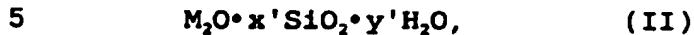
- 1) In the case of using water for washing having a water hardness of from 2 to 6°DH, 25 to 55% by weight of the crystalline alkali metal silicate in the entire composition;
- 15 2) In the case of using water for washing having a water hardness of from 6 to 10°DH, 10 to 45% by weight of the crystalline alkali metal silicate in the entire composition; and
- 3) In the case of using water for washing having a water 20 hardness of from 10 to 20°DH, 5 to 30% by weight of the crystalline alkali metal silicate in the entire composition.

When the content of the crystalline alkali metal silicate is outside the above given range, the washing 25 conditions mentioned above are not likely to be satisfied.

- 35 -

Next, the crystalline alkali metal silicates having the composition ii) above are detailed below.

These crystalline alkali metal silicates are represented by the general formula (II):



wherein M stands for an alkali metal; x' is from 1.5 to 2.6; and y' is from 0 to 20.

Among them, a preference is given to the crystalline alkali metal silicates having x' and y' in the general 10 formula (II) such that each satisfies $1.7 \leq x' \leq 2.2$ and $y' = 0$, and those having a cationic exchange capacity of from 100 to 400 $CaCO_3$, mg/g are usable. The above crystalline alkali metal silicates are one of the materials having ion capturing capacity in the present 15 invention.

Since the crystalline alkali metal silicate usable in the present invention has not only good alkaline effect and alkali buffering capacity but also good ion exchange capacity, the above-mentioned washing conditions are 20 suitably adjusted by adding suitable amounts of the crystalline alkali metal silicate.

The content of the crystalline alkali metal silicate is preferably 4 to 75% by weight in the entire composition, with a particular preference given to the 25 following compositions depending upon the water hardness

- 36 -

of the water for washing used.

- 1) In the case of using water for washing having a water hardness of from 2 to 6°DH, 25 to 55% by weight of the crystalline alkali metal silicate in the entire composition;
- 5 2) In the case of using water for washing having a water hardness of from 6 to 10°DH, 10 to 45% by weight of the crystalline alkali metal silicate in the entire composition; and
- 10 3) In the case of using water for washing having a water hardness of from 10 to 20°DH, 5 to 30% by weight of the crystalline alkali metal silicate in the entire composition.

When the content of the crystalline alkali metal silicate is outside the above given range, the washing conditions mentioned above are not likely to be satisfied.

A method for producing the above crystalline alkali metal silicates is disclosed in Japanese Patent Laid-Open No. 60-227895. However, the crystalline silicates can be generally produced by baking glassy amorphous sodium silicate at a temperature of from 200 to 1000°C. Details of the production method is disclosed in "Phys. Chem. Glasses, 7, pp.127-138 (1966), Z. Kristallogr., 129, pp.396-404(1969)." Also, the crystalline alkali metal silicates are commercially available in powdery or

granular forms under a trade name "Na-SKS-6" ($\delta\text{-Na}_2\text{Si}_2\text{O}_5$) (manufactured by Hoechst).

In the present invention, as in the case for the crystalline alkali metal silicates having the composition

5 i), the crystalline alkali metal silicates having the composition ii) have an average particle size of preferably from 0.1 to 50 μm , more preferably from 1 to 30 μm , still more preferably from 1 to 10 μm .

In the present invention, the crystalline alkali metal silicates having the compositions i) and ii) may be used alone or in combination. It is preferred that the crystalline alkali metal silicates occupy 50 to 100% by weight of the total alkali metal silicates, more preferably 70 to 100% by weight.

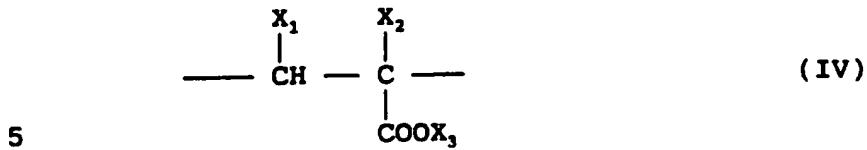
15

(c) Metal Ion Capturing Agents Other Than Alkali Metal Silicates

The metal ion capturing agents other than the alkali metal silicates in the present invention have a calcium ion capturing capacity of not less than 200 CaCO_3 mg/g.

A preference is given to the metal ion capturing agents containing a carboxylate polymer in an amount of not less than 10% by weight. Examples of the above carboxylate polymer include polymers or copolymers, each 25 having repeating units represented by the general formula (IV):

- 38 -



wherein X_1 stands for methyl, a hydrogen atom, or COOX_3 ; X_2 stands for methyl, a hydrogen atom, or hydroxyl; X_3 stands for a hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium, or ethanolamine.

10 In the general formula (IV), examples of the alkali metals include Na, K, and Li, and examples of the alkaline earth metals include Ca and Mg.

15 Examples of the polymers or copolymers usable in the present invention include those obtainable by polymerization reactions of acrylic acid, (anhydrous) maleic acid, methacrylic acid, α -hydroxyacrylic acid, crotonic acid, isocrotonic acid, and salts thereof; copolymerization reactions of each of the monomers; or 20 copolymerization reactions of the above monomers with other polymerizable monomers. Here, examples of the copolymerizable monomers used in copolymerization reaction include aconitic acid, itaconic acid, citraconic acid, fumaric acid, vinyl phosphonic acid, sulfonated maleic acid, diisobutylene, styrene, methyl vinyl ether, ethylene, propylene, isobutylene, pentene, butadiene, isoprene, vinyl acetate (vinyl alcohols in cases where hydrolysis takes place after copolymerization), and 25

- 39 -

acrylic acid ester, without particularly being limited thereto. Incidentally, the polymerization reactions are not particularly limited, and any of the conventionally known methods may be employed.

5 Also, polyacetal carboxylic acid polymers such as polyglyoxylic acids disclosed in Japanese Patent Laid-Open No. 54-52196 are also usable for the polymers in the present invention.

10 In the present invention, the above polymers and copolymers normally have a weight-average molecular weight of from 800 to 1,000,000, preferably from 5,000 to 200,000.

15 Also, in the case of copolymers, although the copolymerization ratio between the repeating units of the general formula (IV) and other copolymerizable monomers is not particularly limited, a preference is given to a copolymerization ratio of the repeating units of general formula (IV)/other copolymerizable monomer = 1/100 to 90/10.

20 In the present invention, the above polymer or copolymer is contained in the composition in an amount of from 1 to 50% by weight, preferably from 2 to 30% by weight, more preferably from 5 to 15% by weight. When the amount of the polymer or copolymer is less than 1% by weight, the effects of the present invention cannot be

- 40 -

obtained, and when the amount exceeds 50% by weight, a further addition of the polymer or copolymer to the composition shows no additional effects, and merely increases the costs thereof.

5 In addition, a highly preferred example of the (c) metal ion capturing agent comprises:

(c-i) the carboxylate polymer mentioned above having a Ca ion capturing capacity of not less than 200 CaCO₃, mg/g; and

10 (c-ii) an aluminosilicate having an ion exchange capacity of not less than 200 CaCO₃, mg/g and having the following formula (III):



wherein M stands for an alkali metal, such as sodium or potassium; x'', y'', and w'' each stands for a molar number of each component; and generally, x'' is from 0.7 to 1.5; y'' is from 0.8 to 6.0; and w'' is from 0 to 20, wherein the weight ratio of (c-i) component to (c-ii) component is (c-i)/(c-ii) = 1/20 to 4/1, preferably 1/9 to 4/1. The total amount of (c-i) and (c-ii) components preferably occupies 70 to 100% by weight based on the (c) metal ion capturing agent.

The aluminosilicates mentioned above may be crystalline or amorphous, and among the crystalline aluminosilicates, a particular preference is given to

- 41 -

those having the following general formula:



wherein y is a number of from 1.8 to 3.0; and w is a number of from 1 to 6.

5 As for the crystalline aluminosilicates (zeolites), synthetic zeolites having an average, primary particle size of from 0.1 to 10 μm , which are typically exemplified by A-type zeolite, X-type zeolite, and P-type zeolite, are suitably used. The zeolites may be used in the forms of
10 powder, a zeolite slurry, or dried particles comprising zeolite agglomerates obtained by drying the slurry. The zeolites of the above forms may also be used in combination.

The above crystalline aluminosilicates are obtainable
15 by conventional methods. For instance, methods disclosed in Japanese Patent Laid-Open Nos. 50-12381 and 51-12805 may be employed.

On the other hand, the amorphous aluminosilicates represented by the same general formula as the above
20 crystalline aluminosilicate are also obtainable by conventional methods. For instance, the amorphous aluminosilicates are prepared by adding an aqueous solution of a low-alkali alkali metal aluminate having a molar ratio of M_2O to Al_2O_3 , (M standing for an alkali metal) of $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1.0$ to 2.0 and a molar ratio of H_2O to

- 42 -

M_2O of H_2O/M_2O = 6.0 to 500 to an aqueous solution of an alkali metal silicate having a molar ratio of SiO_2 to M_2O of SiO_2/M_2O = 1.0 to 4.0 and a molar ratio of H_2O to M_2O of H_2O/M_2O = 12 to 200 under vigorous stirring at normally 15 5 to 60°C, preferably 30 to 50°C.

The intended product can be advantageously obtained by heat-treating a white slurry of precipitates thus formed at 70 to 100°C, preferably 90 to 100°C, for normally not less than 10 minutes and not more than 10 10 hours, preferably not more than 5 hours, followed by filtration, washing and drying. Incidentally, the aqueous solution of an alkali metal silicate may be added to the aqueous solution of a low-alkali alkali metal aluminate.

By this method, the oil-absorbing amorphous 15 aluminosilicate carrier having an ion exchange capacity of not less than 100 $CaCO_3$ mg/g and an oil-absorbing capacity of not less than 80 ml/100 g can be easily obtained (see Japanese Patent Laid-Open Nos. 62-191417 and 62-191419).

Examples of other metal ion capturing agents include 20 aminotri(methylenephosphonic acid), 1-hydroxyethylidene-1,1-diphosphonic acid, ethylenediaminetetra(methylenephosphonic acid), diethylenetriaminepenta(methylenephosphonic acid), and salts thereof; salts of phosphonocarboxylic acids, such as 25 salts of 2-phosphonobutane-1,2-dicarboxylic acid; amino

- 43 -

acid salts, such as salts of aspartic acid and salts of glutamic acid; aminopolyacetates, such as nitrilotriacetates and ethylenediaminetetraacetates.

Examples of other components which may be added to 5 the detergent composition in the present invention as alkalizers besides crystalline and amorphous alkali metal silicates include various compounds including alkali metal salts such as alkali metal carbonates and alkali metal sulfites, and organic amines, such as alkanolamines.

10 In addition, color-fading preventives, and recontamination preventives generally used for detergent compositions, including non-dissociating polymers such as polyethylene glycols, polyvinyl alcohols, and polyvinyl pyrrolidones; organic acid salt builders, such as 15 diglycolates and oxycarboxylates; and carboxymethyl cellulose may be optionally used.

Besides the above, the following components may be 20 also contained in the detergent composition of the present invention. Specifically, the detergent composition of the present invention may contain one or more components selected from enzymes, such as protease, lipase, cellulase, and amylase; caking preventives, such as lower alkylbenzenesulfonates whose alkyl moieties have about 1 to 4 carbon atoms, sulfosuccinates, talc, and calcium

- 44 -

silicates; antioxidants, such as tert-butylhydroxytoluene, and distyrenated cresol; bleaching agents, such as sodium percarbonate; bleaching activators, such as tetraacetyl ethylenediamine; fluorescent dyes; blueing agents; and perfume, without being particularly limited thereto, to give compositions suitable for their purposes.

The detergent compositions of the present invention containing each of the components described above may be produced by any of the conventionally known methods without particular limitation. Examples of the methods for producing high-bulk density detergents include the methods disclosed in Japanese Patent Laid-Open Nos. 61-69897, 61-69899, 61-69900, and 5-209200.

The present invention will be further described by means of the following preparation examples and test examples, without intending to restrict the scope of the present invention thereto.

The measurements shown in Examples are obtained as follows:

20 (1) pH of Washing Liquid

The pH of the washing liquid was measured by adding a detergent composition to the water for washing and then measuring a pH with a glass electrode pH meter (manufactured by HORIBA Ltd.). Here, the pH of the washing liquid refers to the sufficiently stabilized

- 45 -

indicated value.

(2) Amount of Materials Having Ion Capturing Capacity

The ion capturing ability was measured by the following different methods in accordance to a case where 5 the materials used having a metal ion capturing capacity are ion exchange materials and a case where the materials are chelating agents. Incidentally, the ion capturing capacity of the metal ion capturing agents are expressed by CEC (calcium ion exchange capacity) in Tables as in the 10 same manner as in alkali metal silicates.

Ion Exchange Materials

A 0.1 g sample is accurately weighed and added to 100 ml of a calcium chloride aqueous solution (500 ppm concentration, when calculated as CaCO_3), followed by 15 stirring at 25°C for 60 minutes, after which the mixture is filtered using Membrane Filter (made of nitrocellulose; manufactured by Advantech) with 0.2 μm pore size. 10 ml of the filtrate is assayed for Ca content by an EDTA titration, and the calcium ion exchange capacity (cationic 20 exchange capacity) of the sample is calculated from the titer.

Chelating Agents

The calcium ion capturing capacity was measured by the following method using a calcium ion electrode.

25 Incidentally, the solution used herein was prepared with

- 46 -

the following buffer solution:

Buffer: 0.1 M-NH₄Cl-NH₄OH solution (pH 10.0)

(i) Preparation of Calibration Curve

A standard calcium ion solution was prepared and used
5 for obtaining a calibration curve showing the
relationships between the logarithm of the calcium ion
concentration and the voltage, as shown in Figure 1.

(ii) Measurement of Calcium Ion Capturing Capacity

About a 0.1 g sample was weighed into a 100 ml
10 volumetric flask, and the volumetric flask was filled up
to a volume of 100 ml with the above buffer solution. A
CaCl₂ aqueous solution (pH 10.0) having a concentration of
20,000 ppm calculated as CaCO₃, was added dropwise from a
burette in an amount of 0.1 to 0.2 ml for reading each
15 sample voltage. A blank sample was also measured. Thus,
a calcium ion concentration was calculated from the
calibration curve given in Figure 1 by applying a sample
voltage. The calcium ion concentration of the upper line
corresponding to the amount A of samples added dropwise
20 shown in Figure 2 was referred to as calcium ion capturing
capacity.

In the case where the amount of the materials having
an ion capturing capacity was calculated, when using the
water with hardness of 4°DH as in Examples, the ion
25 concentration of the water corresponded to 71.6 CaCO₃, mg/L

- 47 -

(2148 CaCO₃, mg/30 L), the ion concentration corresponding to the water hardness of 0.5°DH being 9.0 CaCO₃, mg/L (270 CaCO₃, mg/30 L). Therefore, in order to adjust the water hardness of the water for washing from 4°DH to 5 0.5°DH, at least a materials having an ion capturing capacity corresponding to an amount of 62.6 CaCO₃, mg/L (1878 CaCO₃, mg/30 L) was necessary. Therefore, the amounts of the material having an ion capturing capacity were expressed using units of CaCO₃, mg/L in Tables.

10 (3) Average Particle Size and Particle Size Distribution of Alkali Metal Silicates

The average particle size and the particle size distribution were measured by using a laser scattering particle size distribution analyzer. Specifically, about 15 200 ml of ethanol was poured into a measurement cell of a laser scattering particle size distribution analyzer ("LA-700," manufactured by HORIBA Ltd.), and about a 0.5 to 5 mg sample was suspended in ethanol. Next, while irradiating ultrasonic wave, the mixture was agitated for 20 one minute, to thereby sufficiently disperse the sample. Thereafter, an He-Ne laser beam (632.8 nm) was irradiated, and the particle size distribution was measured from the diffraction/scattering patterns. The analysis was made based on the combined theories of Fraunhofer diffraction 25 theory and Mie scattering theory. The particle size

- 48 -

distribution of the suspended particles in the liquid was measured in the size range of from 0.04 to 262 μm . The average particle size was a median of the particle size distribution.

5

Preparation Example 1

(Crystalline Alkali Metal Silicates A to E)

To 1000 parts by weight of No. 2 sodium silicate ($\text{SiO}_2/\text{Na}_2\text{O} = 2.5$), 55.9 parts by weight of sodium hydroxide and 8.5 parts by weight of potassium hydroxide were added, followed by stirring using a homomixer to thereby dissolve sodium hydroxide and potassium hydroxide. To this solution, 5.23 parts by weight of finely milled anhydrous calcium carbonate and 0.13 parts by weight of magnesium nitrate hexahydrate were added, and the components were agitated by using a homomixer. A given amount of the mixture was transferred into a nickel crucible and baked in the air at a temperature of 700°C for one hour, followed by rapid cooling. The obtained baked product was milled, to give an alkali metal silicate A in the present invention. This powder was found to have a high ion exchange capacity of 305 CaCO_3 , mg/g.

In the same manner as above, alkali metal silicates B, C, D, and E, each having the composition shown in Table 1, were obtained.

- 49 -

Table 1

5

	M ₂ O	K/Na	y/x	M _{eq} O ₂	z/x	Mg/Ca	CEC CaCO ₃ mg/g
A	Na ₂ O, K ₂ O	0.03	1.8	CaO, MgO	0.02	0.01	305
B	Na ₂ O	—	1.5	CaO	0.2	—	303
C	Na ₂ O, K ₂ O	0.05	2.2	—	—	—	290
D	Na ₂ O	—	2.0	—	—	—	224
E	Na ₂ O	—	4.0	—	—	—	141

10

Preparation Example 2 (Amorphous Aluminosilicate)

15

Sodium carbonate was dissolved in ion-exchanged water, to prepare an aqueous solution with 6% by weight concentration. 132 g of the above aqueous solution and 38.28 g of a sodium aluminate aqueous solution (conc. 50% by weight) were placed in a 1000-ml capacity reaction vessel equipped with baffles. 201.4 grams of a solution of No. 3 Water Glass diluted with water twice were added 20 dropwise to the above mixed solution by under strong agitation at a temperature of 40°C over a period of 20 minutes. Here, the reaction speed was optimized by adjusting a pH of the reaction system to a pH of 10.5 by blowing a CO₂ gas thereinto. Thereafter, the reaction 25 system was heated to a temperature of 50°C and stirred at

- 50 -

50°C for 30 minutes. Subsequently, an excess alkali was neutralized by adjusting a pH of the reaction system to a pH of 9.0 by blowing a CO₂ gas thereinto. The obtained neutralized slurry was filtered under a reduced pressure 5 using a filter paper (No. 5C, manufactured by Toyo Roshi Kaisha, Ltd.). The filtered cake was rinsed with water in an amount of 1000-folds, and the rinsed cake was filtered and dried under the conditions of 105°C, 300 Torr, and 10 hours. The residual portion was dried under the same 10 conditions as above without giving any further rinsing treatments. Further, the dried cake was broken into particles, to give an amorphous aluminosilicate powder in the present invention. Incidentally, the sodium aluminate aqueous solution was prepared by the steps of adding and 15 mixing 243 g of Al(OH)₃, and 298.7 g of a 48% by weight NaOH aqueous solution in a 1000 cc-capacity four-necked flask, heating the mixture to a temperature of 110°C with stirring, and maintaining the temperature of 110°C for 30 minutes, to dissolve the components.

20 As shown by the results of atomic absorption spectrophotometry and plasma emission spectrochemical analysis, the resulting amorphous aluminosilicate had the following composition: Al₂O₃ = 29.6% by weight; SiO₂ = 52.4% by weight; and Na₂O = 18.0% by weight 25 (1.0 Na₂O • Al₂O₃ • 3.10 SiO₂). In addition, the calcium

- 51 -

ion capturing capacity was 185 CaCO₃ mg/g, and the oil-absorbing capacity was 285 ml/100 g. The percentage of the microporous capacity having a microporous diameter of less than 0.1 μ m was 9.4%, and the percentage of the 5 microporous capacity having a microporous diameter of not less than 0.1 μ m and not more than 2.0 μ m was 76.3%. The water content was 11.2% by weight.

Preparation Example 3 (Detergent Compositions)

10 The crystalline alkali metal silicates A to E, the amorphous aluminosilicate, each obtained in the above Preparation Examples, and other components shown in Tables 2 to 11 were used to prepare the detergent compositions of the present invention having the compositions shown in 15 Tables 2 through 11 by the method described below.

Specifically, as for Detergent Compositions 1 through 15 and 17 through 20, given amounts of the aqueous 20 components, including such components as, sodium linear alkylbenzene sulfonate (LAS-Na), sodium alkyl sulfate (AS-Na), No. 1 Sodium Silicate, an acrylic acid-maleic acid copolymer, sodium polyglyoxylate, sodium polyacrylate, sodium citrate, sodium carbonate, sodium sulfate, and sodium sulfite, were prepared as an aqueous 25 slurry of 60% solid content. After spray-drying the slurry, the obtained grains were supplied into Lödige

- 52 -

Mixer, after the remaining powder starting materials were supplied into the mixer, the mixture was subjected to mixing granulation while gradually introducing a liquid nonionic surfactant.

5 As for Detergent Composition 16, the components other than zeolite were prepared as a slurry of 60% solid content, and the slurry was spray-dried to yield grains. The grains were subjected to granulation in High-Speed Mixer after adding a corresponding amount of the zeolite 10 thereinto.

Incidentally, TAED, PC, and enzymes used in each of Detergent Compositions were blended in granular forms.

Thus, powdery detergent compositions with an average particle size of from 300 to 600 μm , each having a bulk 15 density of from 0.6 to 1.0 g/ml were obtained.

Test Example 1

Detergent Compositions 1 through 19 were used to carry out a detergency test under the following 20 conditions:

Preparation of Artificially Stained Cloth

An artificial staining liquid having the following compositions was adhered to a cloth (#2003 calico, 25 manufactured by Senshokushizai Kabushikikaisha Tanigashira

- 53 -

Shoten) to prepare an artificially stained cloth.

Artificial staining liquid was printed on a cloth by an engravure staining machine equipped with an engravure roll coater. The process for adhering the artificial staining 5 liquid to a cloth to prepare an artificially stained cloth was carried out under the conditions of a cell capacity of a gravure roll of 58 cm³/cm², a coating speed of 1.0 m/min, a drying temperature of 100°C, and a drying time of one minute.

10

Composition of Artificial Staining Liquid

	Lauric acid	0.44% by weight
	Myristic acid	3.09% by weight
	Pentadecanoic acid	2.31% by weight
15	Palmitic acid	6.18% by weight
	Heptadecanoic acid	0.44% by weight
	Stearic acid	1.57% by weight
	Oleic acid	7.75% by weight
	Triolein	13.06% by weight
20	n-Hexadecyl palmitate	2.18% by weight
	Squalene	6.53% by weight
	Egg white lecithin crystalline liquid	1.94% by weight
	Kanuma sekigyoku soil	8.11% by weight
25	Carbon black	0.01% by weight
	Tap water	Balance

- 54 -

Detergency Conditions

Washing of the above-mentioned artificially stained cloth in 4°DH water (Ca/Mg = 3/1) was carried out by using Turgotometer at a rotational speed of 100 rpm, at a 5 temperature of 20°C for 10 minutes, in which each of Detergent Compositions given in Tables 2, 4, 6, 8, and 10 was used in concentrations given in Tables 3, 5, 7, 9, and 11, respectively.

Incidentally, the typical water hardness components 10 in the water for washing are Ca^{2+} and Mg^{2+} , whose weight ratios are generally in the range of Ca/Mg = (60-85)/(40-15). Here, a model sample of water of Ca/Mg = 3/1 was used. The unit "°DH" refers to a water hardness which was calculated by replacing Mg with Ca.

15

Calculation of Detergency Rate

Reflectivities of the original cloth and those of the 20 stained cloth before and after washing were measured at 550 μm by means of an automatic recording colorimeter (manufactured by Shimadzu Corporation), and the detergency rate D (%) was calculated by the following equation. The results thereof are shown in Tables 3, 5, 7, 9, and 11.

$$25 \quad D = \frac{(L_2 - L_1)}{(L_0 - L_1)} \times 100(\%),$$

- 55 -

wherein L_0 : Reflectivity of the original cloth;
5 L_1 : Reflectivity of the stained cloth before
washing; and
 L_2 : Reflectivity of the stained cloth after
washing.

Incidentally, the abbreviations and materials shown
10 in Tables 2, 4, 6, 8, 10, 12, and 14 are as follows:

*: Comparative product;
POE: Average molar number of ethylene oxide;
LAS-Na: Sodium linear alkylbenzene sulfonate;
AS-Na : Sodium alkyl sulfate;
15 Acrylic acid-maleic acid copolymer: "SOKALAN CP5,"
(manufactured by BASF Aktiengesellschaft), a
copolymer formed by acrylic acid monomers
and maleic acid monomers, weight-average
molecular weight of 70,000;
Sodium polyacrylate: a polymer of sodium acrylate,
average molecular weight of 10,000;
TAED : Tetraacetyl ethylenediamine;
PC : Sodium percarbonate;
Protease: ALKALI PROTEASE K-16 disclosed in Japanese
20 Patent Laid-Open No. 5-25492;
Cellulase: ALKALI CELLULASE K disclosed in Japanese
Patent Laid-Open No. 63-264699; and
Lipase: LIPOLASE, manufactured by NOVO Nordisk
25 Bioindustry LTD.

- 56 -

Table 2

	(by weight %)	Detergent Composition Nos.			1 - 4 *
		1 - 1	1 - 2 *	1 - 3 *	
Component (a)					
Polyoxyethylene alkylether nC12POE=8	23		36	5	23
Polyoxyethylene alkylether iC12POE=8					
LAS-Na(C12-14)					
AS-Na (C10-18)	7		7	1	7
Soap (C12-18)					
CEC					
Component (b)					
Crystalline Silicate A S/N=1.8	305				
B 1.5	303				
C 2.2	290				
D 2.0	224				
E 4.0	141				
JIS No.1 Sodium Silicate 2.0					
Component (c)					
ZEOLITE 4A	280		25	25	42
Acrylic acid-Maleic acid Copolymer MW=70000	380		8	8	14
Sodium Polyglyoxylate MW=20000	340				
Sodium Polyacrylate MW=10000	220				
Trisodium Citrate 310	310				
		total CEC 208	total CEC 169	total CEC 282	total CEC 209
Other Components					
Amorphous Aluminosilicate	185	4	4	4	4
Sodium Carbonate					
Sodium Sulfate					
Sodium Sulfite					
TAED					
PC					
Protease					
Cellulase					
Lipase					
Water					
(a)+(b)+(c)=	96%	(a)+(b)+(c)= 96%	(a)+(b)+(c)= 96%	(a)+(b)+(c)= 96%	(a)+(b)+(c)= 96%

- 57 -

Table 3
Detergent Composition Nos.

Detergent Concentration (g/L)	Surfactant Conc. (g/L)	1 - 1		1 - 2 *				
		Ion Cap-turing Capacity (CaCO ₃ , mg/L)	pH	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)		
1.00	0.300	208	11.15	68.7	0.430	169	10.85	64.8
0.83	0.249	173	11.03	66.4	0.357	140	10.73	62.4
0.67	0.201	139	10.98	64.2	0.288	113	10.58	50.1
0.50	0.150	104	10.94	63.0	0.215	84	10.48	45.3
0.33	0.099	69	10.72	61.6	0.142	56	10.32	39.6
0.25	0.075	52	10.42	50.6	0.108	42	10.20	35.2

Detergent Concentration (g/L)	1 - 3 *		1 - 4 *					
	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	pH	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	pH	Deter-gency Rate (%)	
1.00	0.06	282	11.45	58.2	0.300	209	10.52	60.2
0.83	0.05	234	11.37	54.3	0.249	173	10.46	53.1
0.67	0.04	189	11.19	50.2	0.201	140	10.38	47.3
0.50	0.03	141	11.01	46.1	0.150	105	10.25	42.1
0.33	0.02	93	10.86	42.8	0.099	69	10.08	38.0
0.25	0.01	71	10.78	30.0	0.075	52	9.62	33.3

- 58 -

Table 4

	(by weight %)	Detergent Composition Nos.		1 - 8 *
		1 - 5 *	1 - 6 *	
Component (a)				
Polyoxyethylene alkylether nC12POE=8	23	23	23	30
Polyoxyethylene alkylether iC12POE=8				
LAS-Na(C12-14)				18
AS-Na (C10-18)	7	7	7	7
Soap (C12-18)				
CEC				
Component (b)				
Crystalline Silicate A S/N=1.8	56			10
B 1.5	303			
C 2.2	290			
D 2.0	224			
E 4.0	141			
JIS No. 1 Sodium Silicate	2.0			
Component (c)				
ZEOLITE 4A	280	8	32	25
Acrylic acid-Maleic acid Copolymer	MW=70000	380	2	14
Sodium Polyglyoxylate	MW=20000	340		
Sodium Polyacrylate	MW=10000	220		
Trisodium Citrate	MW=10000	310		
		total CEC 208	total CEC 154	total CEC 84
Other Components				
Amorphous Aluminosilicate	185	4	4	4
Sodium Carbonate				
Sodium Sulfate				
Sodium Sulfite				
TAED				
PC				
Protease				
Cellulase				
Lipase				
Water				
(a)+(b)+(c)=	96%	(a)+(b)+(c)=	76%	(a)+(b)+(c)= 96% (a)+(b)+(c)= 96%

Table 5

Detergent Concentration (g/L)	Detergent Composition Nos.				
	1 - 5		1 - 6 *		
Surfactant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	pH	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)
1.00	0.300	208	11.43	60.2	0.300
0.83	0.249	173	11.35	58.3	0.249
0.67	0.201	139	11.18	54.6	0.201
0.50	0.150	104	11.00	54.2	0.150
0.33	0.099	69	10.84	45.5	0.099
0.25	0.075	52	10.75	30.1	0.075

Detergent Concentration (g/L)	Detergent Composition Nos.				
	1 - 7 *		1 - 8 *		
Surfactant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	pH	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)
1.00	0.300	154	10.10	50.2	0.550
0.83	0.249	128	9.96	49.3	0.458
0.67	0.201	103	9.81	45.6	0.369
0.50	0.150	77	9.69	41.2	0.275
0.33	0.099	51	9.57	38.1	0.182
0.25	0.075	39	9.13	29.5	0.138

- 60 -

Table 6

	(by weight %)	1 - 9	Detergent Composition Nos.		
			1 - 10	1 - 11	1 - 12
Component (a)					
Polyoxyethylene alkylether nC12POE=8	20		16	18	18
Polyoxyethylene alkylether 1C12POE=8			10	3	3
LAS-Na (C12-14)					
AS-Na (C10-18)					
Soap (C12-18)					
CEC					
Component (b)					
Crystalline Silicate A S/N=1.8	305	33	32	25	25
B 1.5	303				
C 2.2	290				
D 2.0	224				
E 4.0	141				
JIS No.1 Sodium Silicate 2.0					
Component (c)					
ZEOLITE 4A	280	22	21	27	27
Acrylic acid-Maleic acid Copolymer MW=70000	380	7	6		7
Sodium Polyglyoxylate MW=20000	340				
Sodium Polyacrylate MW=10000	220				
Trisodium Citrate 310	310				
		total CEC 215	total CEC 196	total CEC 174	total CEC 166
Other Components					
Amorphous Aluminosilicate	185	14	9	4	4
Sodium Carbonate					
Sodium Sulfate		1	1		
Sodium Sulfite					
TAED				4.5	4.5
PC				9	9
Protease			0.6	0.6	0.6
Cellulase			0.5	0.5	0.5
Lipase		0.1	0.1	0.1	0.1
Water		1.8	3.8	1.3	1.3
(a)+(b)+(c)=82%			(a)+(b)+(c)=85%	(a)+(b)+(c)=80%	(a)+(b)+(c)=80%

Table 7

Detergent Concentration (g/L)	Surfactant Conc. (g/L)	Detergent Composition Nos.			
		1 - 9		1 - 10	
		Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)
		pH			pH
1.00	0.200	215	11.14	64.1	196
0.83	0.166	178	11.01	63.8	163
0.67	0.134	144	10.96	63.6	131
0.50	0.100	108	10.92	63.4	130
0.33	0.066	71	10.68	58.0	98
0.25	0.050	54	10.42	46.5	65
				0.065	49
					10.41

Detergent Concentration (g/L)	Surfactant Conc. (g/L)	Detergent Composition Nos.			
		1 - 11		1 - 12	
		Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)
		pH			pH
1.00	0.210	174	11.00	63.1	166
0.83	0.174	145	10.94	62.5	138
0.67	0.141	117	10.90	61.0	111
0.50	0.105	87	10.86	60.8	105
0.33	0.069	58	10.68	57.9	83
0.25	0.053	44	10.30	45.0	55
				0.053	42
					10.28

- 62 -

Table 8

	(by weight %)	Detergent Composition Nos.		
		1 - 1 3	1 - 1 4	1 - 1 5
Component (a)				
Polyoxyethylene alkylether nC12POE=8		19	19	17
Polyoxyethylene alkylether 1C12POE=8				
LAS-Na (C12-14)				
AS-Na (C10-18)				
Soap (C12-18)				
Component (b)				
Crystalline Silicate A S/N=1.8				
B 1.5	305			
C 2.2	303			
D 2.0	290			
E 4.0	224			
JIS No. 1 Sodium Silicate	141			
JIS No. 1 Sodium Silicate	2.0			
Component (c)				
ZEOLITE 4A	280	8	8	21
Acrylic acid-Maleic acid Copolymer MW=70000	380	25	20	21
Sodium Polyglyoxylate MW=20000	340			
Sodium Polyacrylate MW=10000	220			
Trisodium Citrate	310			
		total CEC 235	total CEC 233	total CEC 138
Other Components				
Amorphous Aluminosilicate	185			4
Sodium Carbonate				
Sodium Sulfate		1	1	1
Sodium Sulfite				
TAED				
PC				
Protease			0.8	0.8
Cellulase			0.6	0.6
Lipase			0.2	0.2
Water			0.4	3.4
(a) + (b) + (c)=97%			(a) + (b) + (c)=97%	(a) + (b) + (c)=90%

Table 9
Detergent Composition Nos.

Detergent Concentration (g/L)	1 - 1 3				1 - 1 4			
	Surfactant Conc. (g/L)	Ion Capturing Capacity (CaCO ₃ , mg/L)	Detergency Rate (%)	Surfactant Conc. (g/L)	Ion Capturing Capacity (CaCO ₃ , mg/L)	Detergency Rate (%)	pH	
1.00	0.220	235	11.31	69.1	0.220	233	11.33	68.7
0.83	0.183	195	11.18	67.2	0.183	193	11.19	66.8
0.67	0.147	157	10.99	66.3	0.147	156	10.98	64.1
0.50	0.110	118	10.95	63.1	0.110	117	10.94	63.1
0.33	0.073	78	10.88	60.4	0.073	77	10.87	60.0
0.25	0.055	59	10.62	48.0	0.055	58	10.64	49.2

Detergent Concentration (g/L)	1 - 1 5			
	Surfactant Conc. (g/L)	Ion Capturing Capacity (CaCO ₃ , mg/L)	pH	Detergency Rate (%)
1.00	0.200	138	11.01	63.5
0.83	0.166	115	10.96	62.3
0.67	0.134	92	10.85	61.2
0.50	0.100	69	10.78	60.0
0.33	0.066	46	10.58	51.2
0.25	0.050	35	10.31	41.6

- 64 -

Table 10

	(by weight %)	Detergent Composition Nos.	
		1 - 1 6*	1 - 1 7*
Component (a)			
Polyoxethylene alkylether nC12POE=8		16	7
Polyoxethylene alkylether iC12POE=8			6
LAS-Na(C12-14)			
AS-Na (C10-18)	20		
Soap (C12-18)	10		
	3	5	
Component (b)			
Crystalline Silicate A S/N=1.8	305		
B	1.5	303	
C	2.2	290	
D	2.0	224	
E	4.0	141	
JIS No. 1 Sodium Silicate	2.0	3	
Component (c)			
ZEOLITE 4Å	280	25	40
Acrylic acid-Maleic acid Copolymer		5	
MW=70000	380		
Sodium Polyglyoxylate	340		
MW=20000		3	
Sodium Polyacrylate	220		
MW=10000			
Trisodium Citrate	310		
		total CEC 89	total CEC 122
			total CEC 116
Other Components	185		
Amorphous Aluminosilicate			
Sodium Carbonate	25	30	7
Sodium Sulfate	3	4	23
Sodium Sulfite	1	1	
TAED			
PC			
Protease	0.5	0.5	0.7
Cellulase	0.4	0.4	0.6
Lipase	0.1	0.1	0.1
Water	4		
		(a)+(b)+(c)=66%	(a)+(b)+(c)=64%
			(a)+(b)+(c)=60%

- 65 -

Table 10 (Continued)

	(by weight %)	Detergent Composition Nos. 1-19*	Detergent Composition Nos. 1-20
Component (a)			
Polyoxyethylene alkylether nC12POE=8		6.5	20
Polyoxyethylene alkylether tC12POE=8		7	
LAS-Na (C12-14)		3	3
AS-Na (C10-18)			
Soap (C12-18)			
	CEC		
Component (b)			
Crystalline Silicate A S/N=1.8	305		
B	1.5	303	
C	2.2	290	
D	2.0	224	2
E	4.0	141	3
JIS No.1 Sodium Silicate	2.0		
Component (c)			
ZEOLITE 4A	280	31	15
Acrylic acid-Maleic acid Copolymer		2.5	3
MW=70000	380		
MW=20000	340		
Sodium Polyglyoxylate			
MW=10000	220		
Sodium Polyacrylate			
MW=10000	310		
Trisodium Citrate			
		total CEC 101	total CEC 210
Other Components			
Amorphous Aluminosilicate	185		2
Sodium Carbonate		10	2
Sodium Sulfate		2	1
Sodium Sulfite		26	
TAED			
PC		0.5	0.7
Protease		0.4	0.5
Cellulase		0.1	0.1
Lipase		6	2.7
Water			
		(a)+(b)+(c)=55%	(a)+(b)+(c)=91%

Table 11 Detergent Composition Nos.

Detergent Concentration (g/L)	Surfactant Conc. (g/L)	1 - 1 6 •			1 - 1 7 •			1 - 1 8 •		
		Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	pH
1.00	0.330	89	10.75	65.1	0.210	122	62.1	0.190	116	10.78
0.83	0.274	74	10.61	62.1	0.174	101	58.9	0.158	96	10.62
0.67	0.221	60	10.55	53.2	0.141	82	50.1	0.127	78	10.45
0.50	0.165	45	10.50	46.2	0.105	61	46.3	0.095	58	10.32
0.33	0.109	29	10.46	41.3	0.069	40	41.0	0.063	38	10.16
0.25	0.083	22	10.29	35.1	0.053	31	33.7	0.048	29	9.91

Detergent Concentration (g/L)	Surfactant Conc. (g/L)	1 - 1 9 •			1 - 2 0		
		Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ , mg/L)	Deter-gency Rate (%)	
1.00	0.165	101	10.36	53.2	0.230	209.6	11.39
0.83	0.137	84	10.12	46.1	0.191	174.0	11.31
0.67	0.111	68	9.81	40.3	0.154	140.4	11.13
0.50	0.082	51	9.62	37.2	0.115	104.8	10.96
0.33	0.054	33	9.51	34.1	0.076	69.2	10.81
0.25	0.041	25	9.12	30.2	0.058	52.4	10.71

As is clear from the results in Tables 2 to 11, when the washing liquids satisfied the washing conditions (1) to (3), provided that the washing liquids do not contain clothes to be washed (Detergent Compositions 1-1, 1-9 through 1-15, and 1-20), high detergency rates were obtained. Particular in the case where detergent compositions had weight ratios of the crystalline alkali metal silicate to the metal ion capturing agent other than the crystalline alkali metal silicate in the ranges of from 5/1 to 1/15, the resulting detergent compositions showed a good detergency of not less than 60%. In addition, even in the case where the washing liquid had a low concentration of the detergent composition of from 0.33 to 0.67 g/L, as exemplified by Detergent Composition No. 1-1 in Table 3, a high detergency rate of not less than 60% was maintained. This means that since the standard amount of dosage of the conventional products for one wash is 25 to 30 g/30 L, the present invention product has been further made compact 0.4 to 0.7 times those of conventional compact detergents.

By contrast, as for the washing liquids which did not satisfy the washing conditions (1) to (3) mentioned above (Detergent Compositions 1-2 through 1-8, and 1-16 through 1-19), in the case where the washing liquid had a low concentration of the detergent composition of from 0.33 to

- 68 -

0.67 g/L, only low detergency rates were achieved.

Test Example 2

Detergent Compositions shown in Table 12 were used to
5 carry out a detergency test under the following
conditions:

The same washing procedures as in Test Example 1 were
carried out except that the washing temperature was
changed to 30°C, and that the water used for washing was
10 changed to that having a water hardness of 8°DH
(Ca/Mg = 3/1), at detergent concentrations shown in Table
13. The results are shown in Table 13.

- 69 -

Table 12

	C E C	Detergent Composition Nos.	
		2 - 1	2 - 2 *
Component (a)			
LAS (C12)		4.00	5.00
AS (C14-15)		12.50	20.00
Soap (C12-20)			
Polyoxyethylene alkylether			
nC12-14 POE=8			
Component (b)			
Crystalline Silicate A	305	28.00	10.00
B	303		
C	290		
D	224		
E	141		
Sodium silicate	0		
Component (c)			
Acrylic acid-maleic acid			
Copolymer	MW=70000	380	4.00
Zeolite		280	40.00
Sodium Polyglyoxylate	MW=20000	340	
Sodium Polyacrylate	MW=10000	220	
Trisodium Citrate		310	
Other Components			
Amorphous Aluminosilicate		185	3.50
Sodium Carbonate			11.00
Sodium Sulfate			4.0
Sodium Sulfite			0.50
TAEDE			
Sodium Percarbonate			
Protease			0.90
Cellulase			0.90
Lipase			0.90
Other Components			1.80
Total (%)		100.00	100.00
Surfactant (a)		16.50	25.00
Alkali Metal Silicates (b)		28.00	10.00
Other Builders (c)		44.00	45.00
(a) + (b) + (c) =		88.50	80.00
Ion Capturing Capacity (TOTAL CEC)		219.08	181.85

- 70 -

Table 13

Detergent Concentration (g/L)	Detergent Composition Nos.					
	2 - 1			2 - 2 *		
	Surfactant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ mg/L)	Deter-gency Rate (%)	Surfac-tant Conc. (g/L)	Ion Cap-turing Capacity (CaCO ₃ mg/L)	Deter-gency Rate (%)
2.00	0.330	438.2	11.32	75.8	0.500	363.7
1.50	0.248	328.6	11.19	70.7	0.375	272.8
1.20	0.198	262.9	11.10	68.0	0.300	218.2
1.00	0.165	219.1	11.00	66.1	0.250	181.9
0.83	0.137	181.8	10.94	63.3	0.208	150.9
0.67	0.111	146.8	10.88	60.4	0.168	121.8
0.50	0.083	109.5	10.69	52.1	0.125	90.9
0.33	0.054	72.3	10.38	46.4	0.083	60.0
						9.51
						35.1

- 71 -

As is clear from Table 13, when the washing liquid (Detergent Composition No. 2-1) satisfied the washing conditions (1) to (3), a high detergency rate was obtained. By contrast, as for the washing liquid 5 (Detergent Composition 2-2) which did not satisfy the washing conditions (1) to (3) mentioned above, in the case where the washing liquid had a low concentration of the detergent composition of from 0.50 to 1.20 g/L, only a low detergency rate was achieved.

10

Test Example 3

Detergent Compositions shown in Table 14 were used to carry out a detergency test under the following conditions:

15 The same washing procedures as in Test Example 1 were carried out except that the washing time was changed to 30 minutes, that the washing temperature was changed to 40°C, and that the water used for washing was changed to that having a water hardness of 15°DH (Ca/Mg = 3/1), at 20 detergent concentrations shown in Table 15. The results are shown in Table 15.

- 72 -

Table 14

	C E C	Detergent Composition Nos.	
		3 - 1	3 - 2 *
Component (a)			
LAS (C12)		3.00	3.00
AS (C14-15)		10.40	18.40
Soap (C12-20)			
Polyoxyethylene alkylether nC12-14 POE=8			
Component (b)			
Crystalline Silicate A	305	20.00	8.00
B	303		
C	290		
D	224		
E	141		
Sodium silicate	0		
Component (c)			
Acrylic acid-maleic acid			
Copolymer	MW=70000	380	9.00
Zeolite		280	44.00
Sodium Polyglyoxylate	MW=20000	340	
Sodium Polyacrylate	MW=10000	220	
Trisodium Citrate		310	3.00
Other Components			
Amorphous Aluminosilicate	185	3.00	10.00
Sodium Carbonate		3.00	3.00
Sodium Sulfate		0.50	0.50
Sodium Sulfite			
TAED			
Sodium Percarbonate		0.60	0.60
Protease		0.60	0.60
Cellulase		0.60	0.60
Lipase		2.30	3.30
Other Components			
Total (%)		100.00	100.00
Surfactant (a)		13.40	21.40
Alkali Metal Silicates (b)		20.00	8.00
Other Builders (c)		56.00	52.00
(a) + (b) + (c) =		59.40	81.40
Ion Capturing Capacity (TOTAL CEC)		233.25	198.40

Table 15

Detergent Concentration (g/L)	Detergent Composition Nos.					
	3 - 1			3 - 2*		
Surfactant Conc. (g/L)	Ion Capturing Capacity (CaCO ₃ , mg/L)	Detergency Rate (%)	Surfactant Conc. (g/L)	Ion Capturing Capacity (CaCO ₃ , mg/L)	Detergency Rate (%)	Detergency Rate (%)
4.00	0.536	933.0	11.26	76.1	0.856	793.6
3.00	0.402	699.8	11.14	73.4	0.642	595.2
2.50	0.335	583.1	11.02	70.2	0.535	496.0
2.00	0.268	466.5	10.91	67.2	0.428	396.8
1.50	0.201	349.9	10.74	63.6	0.321	297.6
1.20	0.161	279.9	10.66	60.2	0.257	238.1
1.00	0.134	233.3	10.56	51.3	0.214	198.4
0.83	0.111	193.6	10.45	43.2	0.178	164.7
0.67	0.090	156.3	10.32	38.6	0.143	132.9
						9.50
						20.1

- 74 -

As is clear from Table 15, when the washing liquid (Detergent Composition No. 3-1) satisfied the washing conditions (1) to (3), a high detergency rate was obtained. By contrast, as for the washing liquid 5 (Detergent Composition 3-2) which did not satisfy the washing conditions (1) to (3) mentioned above, in the case where the washing liquid had a low concentration of the detergent composition of from 0.80 to 2.50 g/L, only a low detergency rate was achieved.

10

INDUSTRIAL APPLICABILITY

According to the washing method and the clothes detergent composition of the present invention, since the surfactant concentration can be kept low and the washing 15 power is excellent, the standard amount of dosage of the detergent is remarkably smaller than the conventional compact clothes detergent composition. In addition, since the detergent composition is phosphorus-free, the detergent composition is less susceptible to cause 20 environmental problems.

The present invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such 25 modifications as would be obvious to one skilled in the

- 75 -

art are intended to be included within the scope of the following claims.

- 76 -

CLAIMS

1. A clothes washing method using a phosphorus-free clothes detergent composition comprising a surfactant, an 5 alkali metal silicate, and a metal ion capturing agent other than the alkali metal silicate, the weight ratio of the alkali metal silicate to the metal ion capturing agent other than the alkali metal silicate being not more than 5/1, the method comprising the step of washing clothes in 10 a washing liquid having the following washing conditions:

(1) The washing liquid having a pH of not less than 10.60;

(2) The washing liquid containing a material having 15 an ion capturing capacity in an amount sufficient for theoretically changing a water hardness of water for washing to be not more than 0.5°DH; and

(3) The washing liquid having a surfactant concentration of from 0.07 to 0.17 g/L.

20 2. The washing method according to claim 1, wherein the concentration of the detergent composition in the washing liquid is from 0.33 to 0.67 g/L for the water for washing with 2 to 6°DH.

25 3. The washing method according to claim 1, wherein

- 77 -

the concentration of the detergent composition in the washing liquid is from 0.50 to 1.20 g/L for the water for washing with 6 to 10°DH.

5 4. The washing method according to claim 1, wherein the concentration of the detergent composition in the washing liquid is from 0.80 to 2.50 g/L for the water for washing with 10 to 20°DH.

10 5. A phosphorus-free clothes detergent composition comprising components (a) to (c):

- (a) a surfactant;
- (b) an alkali metal silicate; and
- (c) a metal ion capturing agent other than component

15 (b),
wherein a total amount of (a), (b), and (c) components occupies 70 to 100% by weight of the entire composition, and wherein the weight ratio of component (b) to component (a) is $b/a = 9/1$ to $1/2$, and the weight ratio of component (b) to component (c) is $b/c = 5/1$ to $1/15$.

20 6. The clothes detergent composition according to claim 5, wherein the weight ratio of component (b) to component (a) is $b/a = 9/1$ to $9/11$, and the weight ratio of component (b) to component (c) is $b/c = 4/1$ to $1/15$.

- 78 -

7. The clothes detergent composition according to claim 5 or 6, wherein the surfactant contains a nonionic surfactant in an amount of 50 to 100% by weight.

5

8. The clothes detergent composition according to claim 7, wherein the nonionic surfactant is a polyoxyethylene alkyl ether having an ethylene oxide moiety with an average molar number of from 5 to 15 and an alkyl moiety with average carbon atoms of from 10 to 18.

10

9. The clothes detergent composition according to any one of claims 5 to 8, wherein the alkali metal silicate is contained as an alkalizer in an amount of 50 to 100% by weight of the entire alkalizer.

15

10. The clothes detergent composition according to any one of claims 5 to 9, wherein the ratio of $\text{SiO}_2/\text{M}_2\text{O}$ for the alkali metal silicate, M standing for an alkali metal, is from 0.5 to 2.6.

20

11. The clothes detergent composition according to any one of claims 5 to 10, wherein the alkali metal silicate is crystalline.

25

- 79 -

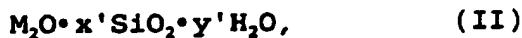
12. The clothes detergent composition according to
claim 11, wherein the crystalline alkali metal silicate is
represented by the following formula (I):



5 wherein M stands for an element in Group Ia of the
Periodic Table; Me stands for one or more elements
selected from the group consisting of Group IIa, IIb,
IIIa, IVa, and VIII; y/x is 0.5 to 2.6; z/x is 0.01 to
1.0; n/m is 0.5 to 2.0; and w is 0 to 20.

10

13. The clothes detergent composition according to
claim 11, wherein the crystalline alkali metal silicate is
represented by the following formula (II):



15 wherein M stands for an alkali metal; x' is 1.5 to 2.6;
and y' is 0 to 20.

20 14. The clothes detergent composition according to
any one of claims 5 to 13, wherein the (c) metal ion
capturing agent contains a carboxylate polymer having a Ca
ion capturing capacity of not less than 200 CaCO₃ mg/g in
an amount of not less than 10% by weight.

25 15. The clothes detergent composition according to
any one of claims 5 to 14, wherein the (c) metal ion

- 80 -

capturing agent comprises:

(c-i) a carboxylate polymer having a Ca ion

capturing capacity of not less than 200 CaCO₃ mg/g; and

(c-ii) an aluminosilicate having an ion exchange

5 capacity of not less than 200 CaCO₃ mg/g and having the following formula (III):



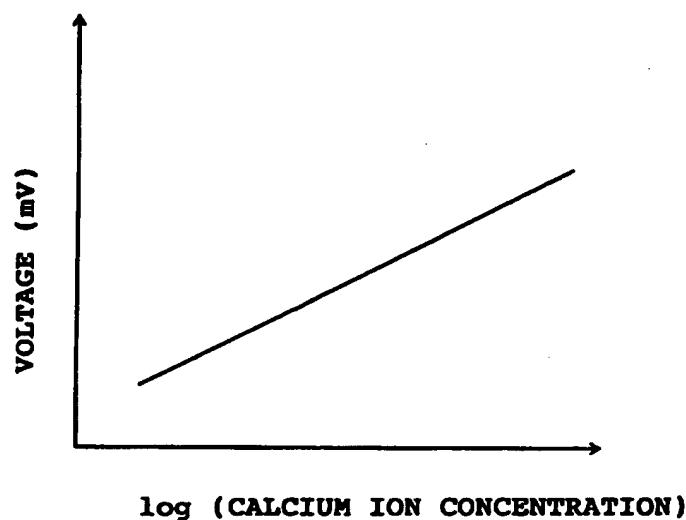
wherein M stands for an alkali metal; x'', y'', and w'' each stands for a molar number of each component; x'' is from

10 0.7 to 1.5; y'' is from 0.8 to 6.0; and w'' is from 0 to 20, and wherein the weight ratio of (c-i) component to (c-ii) component is (c-i)/(c-ii) = 1/20 to 4/1, and the total amount of (c-i) and (c-ii) components occupies 70 to 100% by weight based on the (c) metal ion capturing agent.

15

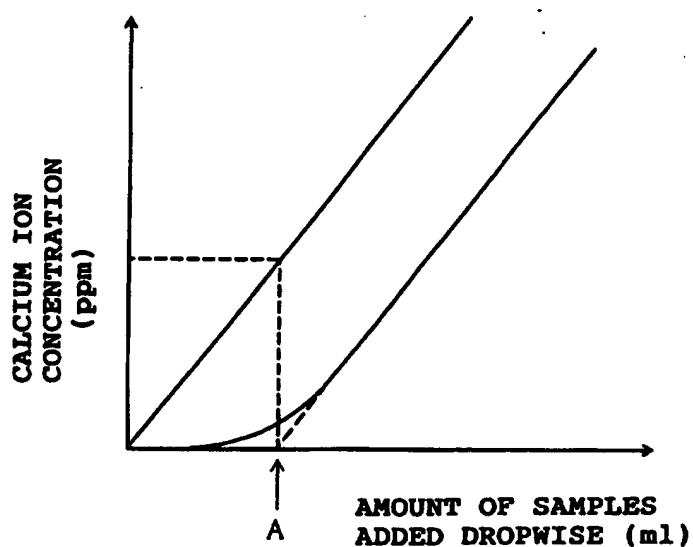
16. The washing method according to claim 1, wherein the clothes detergent composition according to any one of claims 5 to 15 is used.

1 / 1



log (CALCIUM ION CONCENTRATION)

F I G. 1



CALCIUM ION CONCENTRATION (ppm)

AMOUNT OF SAMPLES ADDED DROPOWISE (ml)

A

F I G. 2

INTERNATIONAL SEARCH REPORT

Internal Application No
PCT/JP 95/01750A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/08 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	EP,A,0 657 528 (PROCTER & GAMBLE) 14 June 1995 see page 4, line 10 - line 14; claims 1,4 see page 3, line 37 - page 4, line 9 ---	5, 10, 11, 13
A		12, 15
X	EP,A,0 551 670 (UNILEVER) 21 July 1993 see page 3, line 43 - line 55 see page 4, line 20 - page 5, line 38; claim 10; table 1 see page 6, line 41 - line 43 ---	5, 7, 8, 10
A		1
X	EP,A,0 512 371 (DISPO-KOMMERZ) 11 November 1992 see claims 1,2 ---	5
X	US,A,4 303 556 (R. A. LLENDADO) 1 December 1981 see claim 1 ---	5
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- 'A' document defining the general state of the art which is not considered to be of particular relevance
- 'B' earlier document but published on or after the international filing date
- 'C' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- 'O' document referring to an oral disclosure, use, exhibition or other means
- 'P' document published prior to the international filing date but later than the priority date claimed

'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

'A' document member of the same patent family

1

Date of the actual completion of the international search

12 January 1996

Date of mailing of the international search report

19-01-1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentstaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+ 31-70) 340-3016

Authorized officer

Van Bellingen, I

INTERNATIONAL SEARCH REPORT

Internat'l Application No
PCT/JP 95/01750

C(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO,A,92 07928 (HENKEL) 14 May 1992 see page 3, paragraph 2 see page 4, paragraph 4; claims 1,2,4 & JP-06502199T cited in the application ---	5,10,14
A	EP,A,0 550 048 (KAO) 7 July 1993 see claims 1,5,8,11 & JP,A,06116588 cited in the application ---	5-15
A	EP,A,0 289 767 (DEGUSSA) 9 November 1988 see claim 1 ---	5
A	PATENT ABSTRACTS OF JAPAN vol. 18 no. 052 (C-1158) ,27 January 1994 & JP,A,05 271700 (KAO) 19 October 1993, see abstract -----	5

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Internat'l Application No

PCT/JP 95/01750

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-657528	14-06-95	WO-A-	9516018	15-06-95
EP-A-551670	21-07-93	US-A- AU-B- CA-A-	5281351 2986592 2084172	25-01-94 10-06-93 07-06-93
EP-A-512371	11-11-92	DE-A-	4114956	05-11-92
US-A-4303556	01-12-81	US-A- CA-A- JP-A-	4180485 1101299 54108813	25-12-79 19-05-81 25-08-79
WO-A-9207928	14-05-92	DE-A- AT-T- DE-D- EP-A- JP-T- TR-A- US-A-	4034131 125861 59106172 0554287 6502199 25381 5393455	30-04-92 15-08-95 07-09-95 11-08-93 10-03-94 01-03-93 28-02-95
EP-A-550048	07-07-93	JP-A- JP-A- JP-A- JP-A- JP-A- JP-A- JP-A- JP-A- AU-B- US-A- JP-A- JP-A- JP-A-	6116588 6116589 6116590 6116600 6116591 6116592 5184946 3042192 5427711 6172794 6200291 5279013	26-04-94 26-04-94 26-04-94 26-04-94 26-04-94 26-04-94 27-07-93 01-07-93 27-06-95 21-06-94 19-07-94 26-10-93
EP-A-289767	09-11-88	DE-A- JP-A-	3715052 63287550	17-11-88 24-11-88